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**METHOD OF PRODUCING A SILVER ALLOY PART AND ALLOY USED  
FOR SAME**

5 The present invention relates to the field of metal alloys. More particularly it relates, on the one hand, to a method for obtaining a part made of an alloy based on silver (Ag) and, on the other hand, to the base alloy used to achieve this.

10 Silver-based alloys are commonplace. For example silver is mixed with a few tenths of a percent of magnesium (Mg) and nickel (Ni), the latter metal acting as grain refiner. By internal oxidation of the magnesium into magnesium oxide (MgO), this alloy becomes very hard and  
15 has useful mechanical properties. In addition, and unlike purely metallic alloys, its hardness and its grain size are preserved after high-temperature treatments, such as brazing. It is also an excellent conductor. Such properties particularly destine it to be used for example  
20 in electrical contact springs, in certain jewelry parts, such as clasps, and in high-temperature superconducting cable jackets.

However, the presence of nickel is a serious drawback  
25 since this metal is highly allergenic, which greatly limits its use in jewelry. Moreover, it has been found that nickel is a poison for superconducting materials, and an Ag-Mg-Ni alloy cannot be used directly in the jackets for high-temperature superconducting cables. As  
30 disclosed in the document EP-02405215.1 in the name of the Applicant, it is therefore necessary to insert a layer of pure silver between the alloy layer and the superconducting cable.

35 In the current state of the art, to manufacture conventional Ag-Mg-Ni alloy parts, the various

constituents are for example induction-melted in a graphite crucible and then the liquid is poured into a steel or graphite mold. The ingot is then cold-deformed or hot-deformed into the desired form and exposed to a stream of air or oxygen at a temperature that may vary from 650 to 730°C, which causes the magnesium to oxidize to MgO. This operation hardens the alloy while still maintaining, thanks to the presence of nickel, which acts as a refiner, grains smaller in size than 20 µm.

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To avoid the abovementioned problems caused by the presence of nickel, it would be conceivable simply to apply the same method to a silver/magnesium mixture.

15 Document GB 866 082 discloses a method for the direct oxidation of magnesium in an Ag-Mg alloy. However, if such an operation is carried out, the resulting alloy has coarse grains, making it brittle and unsuitable for the intended applications. To illustrate the foregoing, Figure 1 shows a metallographic section of an Ag-Mg (0.9 at% Mg) alloy sheet that has been exposed for 1 h to a stream of oxygen at a temperature of 650°C. Observations and measurements made show that the outer layers 10 of the sheet undergo oxidation and have a high Vickers hardness of around 155, compared with the starting alloy of 50 hardness. However, it should be noted that the size of the constituent grains of the alloy is around 50 µm.

20 The object of the present invention is to provide an alloy that has the same properties as Ag-Mg-Ni, particularly due to its fine grain size, but does not have the abovementioned drawbacks.

30 More precisely, the invention relates to a method of producing a part made of a silver-based alloy, characterized in that it consists in taking an initial

alloy containing silver and at least one metal soluble in silver at contents of between 0.04 and 4 at% and capable of forming a stable oxide at high temperature, and then carrying out in succession the following operations:

- 5       - oxygenation of the initial alloy so as to dissolve oxygen into the silver that it contains;
- partial oxidation of the soluble metal so as to form precipitate particles that prevent the alloy grains from coarsening; and
- 10       - complete oxidation, on at least an outer layer, of the soluble metal into an oxide stable at high temperature.

Advantageously, the oxygenation is carried out by  
15 exposing the initial alloy to a stream of oxygen at a temperature of about 300°C.

According to a first embodiment, the initial alloy is a part having the desired final form. In this case, the  
20 complete oxidation takes place straight after the partial oxidation.

According to a second embodiment, the initial alloy is a part having an intermediate form, such as a wire, a tube  
25 or a strip. In this case, the partial oxidation is carried out by placing the oxygenated part for about one hour in an inert atmosphere or in a vacuum, at a temperature of between 400 and 850°C. The part is then made into its final form before the complete oxidation.

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According to a third embodiment, the initial alloy is in the form of powder. In this case, the powder is compacted before the oxygenation, so as to preserve an open porosity over its entire thickness. The part thus  
35 obtained is extruded hot, which causes it to undergo partial oxidation. It is then made into its final form

before the complete oxidation.

According to a fourth embodiment, which constitutes a simple variant of the third embodiment, the initial alloy  
5 is also in powder form, but this powder is compacted after the oxygenation.

In all cases, the complete oxidation is carried out by exposing the part to an oxidizing atmosphere at a  
10 temperature of between 400 and 850°C.

The invention also relates to a silver-based alloy, characterized in that it contains at least one metal which is soluble in silver and capable of forming a  
15 stable oxide at high temperature, and which, by internal oxidation, hardens it, while still providing a final grain size of less than 20  $\mu\text{m}$ .

Advantageously, the metal alloyed with the silver is  
20 selected from magnesium, aluminum, titanium, gallium, manganese and zinc, or a combination of these metals. The content is between 0.04 and 4 at%.

Other features of the invention will become apparent from  
25 the description that follows, given with reference to the appended drawing, in which Figures 2 and 3 are metallographic sections of Ag-Mg alloy sheets, after the oxygenation step and after the complete oxidation according to the invention, respectively.

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A first method of implementing the invention starts with a part made of a simple Ag-Mg alloy in the desired final form. The alloy used is generally in the work-hardened state, with a section reduction ratio of around 50 to  
35 95%. The optional prior heat treatments were carried out in an inert or reducing atmosphere, at temperature low

enough to preserve a fine grain structure. Typically, the various operations lasted one hour at a temperature of about 500°C. The alloy has a magnesium content equal to that intended for the final application. In general, this  
5 content is between 0.04 and 4 at%.

The first phase of the method consists in oxygenating the part. For this purpose, a stream of oxygen flows in contact with it at a temperature of about 300°C for long  
10 enough to obtain the desired penetration. Typically, this duration is 24 hours for a penetration of 50 microns, but it may be shortened if the oxygen partial pressure is increased. Under these conditions, the oxygen diffuses into the part and dissolves in the silver without  
15 appreciably oxidizing the magnesium. The hardness of the alloy does not increase and its fine grain structure remains.

Figure 2 clearly shows the effect of this oxygenation on a sheet of Ag-Mg (0.9 at% Mg) alloy. The outer layers  
20 of small, less than 20  $\mu\text{m}$ , grain size may be distinguished. Moreover, the Vickers hardness measurement gives a value of 57 for the outer layers and 51 for the central layer 14. Next, in a second phase, the part is  
25 placed in a stream of air or oxygen, at a temperature of between 400 and 850°C, preferably about 600°C. The magnesium is then oxidized to MgO. The duration of this phase depends on the temperature, the oxygen partial pressure and the thickness of the oxide layer desired.

30 However, if the oxidation process thus carried out is examined in greater detail, it will be seen that it comprises two phases. Firstly, the oxygen dissolved in the silver during the oxygenation step immediately  
35 oxidizes some of the magnesium. Since the amount of oxygen dissolved in the silver is insufficient to oxidize

all the magnesium present in the alloy, the oxidation is therefore partial and precipitate particles are formed that are inserted into the matrix of the alloy and prevent coarsening of the Ag-Mg grains by blocking their grain boundaries. Immediately after this, the oxygen present in the atmosphere continues the oxidation of the magnesium for a certain time, so as to oxidize at least an outer layer of it. The alloy therefore hardens but, thanks to the presence of the precipitate particles that act as dispersoids, the size of these grains is less than 20  $\mu\text{m}$ .

This result is illustrated in Figure 3. The outer layers that were oxygenated during the first phase of the method have, after oxidation, fine grains with a size of less than 20  $\mu\text{m}$ . The central layer was not oxygenated and, to underline the contribution of the oxygenation phase, it was oxidized during the second phase. Thus, the central region can be directly compared with Figure 1. Its hardness is that of an Ag-MgO alloy, but the grains are coarse and make the material brittle. The Vickers hardness measurement gives a value of 136 for the outer layers and 147 for the center.

For practical use, if the prior oxygenation is not carried out over the entire thickness of the part, it is therefore important for the oxidation to take place to a depth equal to or less than that of the oxygenated layer, so as to avoid any risk of fracture.

The alloy thus obtained has properties similar to a conventional Ag-Mg-Ni alloy but, since it contains no nickel, it is not allergenic and does not contaminate high-temperature superconducting materials. However, the alloy produced is very hard and therefore cannot be easily formed.

A second method of implementing the invention starts with an intermediate part, for example in the form of a wire, tube or strip, made of an Ag-Mg alloy. This part firstly  
5 undergoes, as in the first method of implementation, an oxygenation phase.

Next, the two oxidation phases are separated, only the partial oxidation being firstly carried out. For this  
10 purpose, the part is placed for about one hour in a vacuum or in an inert atmosphere (for example nitrogen or argon) at a temperature of between 400 and 850°C. As previously, an MgO precipitate forms that prevents the alloy grains from coarsening.

15 At this point in the method, the part is still malleable and it is then given its final form, for example by rolling, drawing, deep-drawing, cutting, bending, stamping, etc., these techniques being well known to  
20 these skilled in the art.

Only then is the oxidation of the magnesium to MgO completed, under conditions similar to those mentioned above. The alloy then hardens, without the grains  
25 coarsening.

A third method of implementing the invention starts with a silver-magnesium alloy in powder form, which is then compacted, while still maintaining an open porosity over  
30 its entire thickness, in an intermediate form, for example a cylindrical billet 100 mm in diameter and 500 mm in length. As in the first method of implementation, the part then undergoes an oxygenation phase.

35 In the next operation, the compacted part undergoes hot

extrusion. To do this, it is firstly preheated to a temperature of between 400°C and 850°C in an inert atmosphere, which automatically initiates the partial oxidation phase. The extrusion and final forming operations are then carried out on the part before, lastly, the complete magnesium oxidation step is carried out.

It should be noted that, according to a fourth method of implementing the invention, which constitutes a variant of the third method of implementation, the oxygenation phase may perfectly well be carried out before the alloy is compacted.

The present description has been given with reference to the use, at the start of the method, of an Ag-Mg alloy whose magnesium content is between 0.04 and 4 at%. However, it goes without saying that the magnesium may be partly or completely replaced with any silver-soluble metal with the abovementioned contents and capable of hardening it by forming an oxide that is stable at high temperature. Moreover, to provide a material having acceptable mechanical properties, these elements must, in the oxidized state, provide alloy grains of a size smaller than 20  $\mu\text{m}$ . Thus, for example, it is possible to use, among other metals, aluminum, titanium, gallium, manganese or zinc.

Thus, a method is provided that results in a silver-based alloy that is made very hard thanks to the presence of a metal oxide, yet still has a particularly small grain size. The resulting alloy may be particularly used for certain jewelry parts, without incurring any particular risk of an allergy, or in jackets for high-temperature superconducting cables, without contaminating the superconducting material.